WETTABILITY ENHANCEMENT OF POLYMERIC AND GLASS MICRO FIBER REINFORCEMENT BY PLASMA TREATMENT

TREJBAL Jan[1], ŠMILAUER Vít[1], KROMKA Alexander[1,2], POTOCKÝ Štěpán[2], KOPECKÝ Lubomír[1]

[1]Czech Technical University in Prague, Faculty of Civil Engineering, Prague, Czech Republic, EU,
jan.trejbal@fsv.cvut.cz
[2]Czech Academy of Science, Institute of Physic, Prague, Czech Republic, EU

Abstract

Plasma treatments were used to modify surface properties of polyethylene terephthalate (PET) and glass micro fibers, to improve their wettability. PET fibers, having diameter of 400 μm, and glass fibers (ø14 μm) were exposed to low pressure oxygen plasma. A direct horizontal optical method was used for contact angle measurements on fiber surfaces submerged into distilled water. Surface morphology changes before and after treatment were characterized by scanning electron microscopy. Finally, cement paste specimens reinforced with PET and lime-based mortars reinforced with glass fibers were made and after 28 days of mixture curing tested by four-point bending tests. After oxygen plasma treatment contact angles decreased by 60 % on PET fibers and by 25 % on glass fibers in comparison with untreated fibers. Next, SEM images revealed the significant surface damages of PET fibers and minor damages of glass fibers. Both four-point tested samples reinforced with treated fibers exhibited the maximum bending strength loss about to 10 to 20 percent compared to samples with untreated reinforcement. The samples reinforced with untreated PET fibers exhibited the deflection-softening, while the samples with plasma treated fibers deflection-hardening.

Keywords: Plasma Treatments; Cool Oxygen Plasma; Wettability; Contact Angle; Micro Fibers

1. INTRODUCTION

Usage of man-made micro fibers to reinforce bulk material properties become a common in majority of industry fields. A small bulk property improvement has strong impact in civil engineering due to mass production [1]. Fiber-reinforced materials exhibit good mechanical properties, e.g. high mechanical resistance (abrasion, impact resistance), ductility, water resistance etc. [2, 3]. The main task of the micro fiber addition is the distribution of shrinkage into several small cracks in the case of materials based on shrinking binders (mainly lime and cement), and to prevent the single crack openings after linear elastic response in the case of loaded samples [1]. In the civil engineering, the micro fiber reinforcement (MFR) is the most often used for a) production of watertight concretes and concretes exposed to risk of steel reinforcement corrosion (absence of cracks disallows water penetration), and b) for production of large-scale construction exposed to temperature or moisture changes, dynamic loads, point loads (MFR provides a compactness - hence usability - of materials after the crossing the material loading capacity) [4].

MFR can be classified by fibers material, diameter, tensile strength and their modulus of elasticity. As material, polymeric or glass can be used. Both polymeric (in particular PET, PVA, PP) and glass MFRs have high tensile strength equal to about hundred or even thousands MPa. Their diameter is equal to tens or hundreds micrometers. Other characteristic property is low ratio of diameter to length (and related high specific surface enabling better stress transferring from matrix to fibers) and favorable cost [5, 6]. Polymeric and glass fibers reveal low surface wettability (hydrophobicity). On the other hand, MFR requires good adhesion between the fiber surface and matrix. To improve the mechanical strength of reinforced materials, adhesion between the fiber surfaces and matrix must be ensured [7].

The mechanical strength can be modified by fiber surface treatment by mechanical, chemical and physical methods [8, 9, 10, 11]. Currently, the newly introduced plasma treatment becomes popular as progressive physical method. The low pressure plasma treatment represents a universal, efficient and eco-friendly alternative for surface modifications. Plasma can be defined as ionized gas (composed of electrons, ions, and

neutral species). The mechanism for plasma surface modification relays on surface atoms replacement by oxygen atoms and formation of polar groups. The presence of polar or functional chemical groups enhances the reactivity with the matrix based on cement or lime binder (both contain water).

In the present work we report on the modification of polyethylene terephthalate (PET) and glass fibers by oxygen plasma treatment. The influence of plasma treatment on contact angle, fiber morphology and loading tests of composite materials reinforced with such modified fibers is studied.

2. MATERIALS AND METHODS

2.1. Micro fibers

Two different types of fibers were used: PET and glass. The PET fibers (made by Spokar in the Czech Republic) having diameter equal to 400 μm were chopped to about 10 to 15 mm length from original length of 1200 mm. The glass fibers AntiCrack HD (made by Cem-Fil® in Spain) had diameter 14 μm and length of 12 mm. These fibers having industrial water flushable sizing were primary made for reinforcement of concrete or mortars to avoid shrinkage crack formation during hardening. Fiber properties are summarized in **Table. 1**.

Table 1 Basic fiber parameters

Fiber	Tensile strength [MPa]	Modulus of elasticity [GPa]	Density [kg/m3]	Diameter [μm]	Length [mm]
PET	~ 650	~ 10	1340	400	10-15
Glass	3500	72	2680	14	12

2.2. Cement matrix with PET fibers

Portland cement (CEM I 42.5 R, Radotín in the Czech Republic) was used for the production of the tested cement matrix specimens in a macro scale. All cement mixtures had the same water to cement ratio equal to 0.4. Fiber amount in the reinforced samples was 2 wt. % of the cement paste. Three sample types were prepared: cement paste without reinforcement (labeled as CR) as the reference material, the mixture containing untreated fibers (CF), and the mixture containing plasma treated fibers (CFP).

2.3. Lime-based matrix with glass fibers

Lime (CL 90, Tmaň in the Czech Republic) and metakaolin (PKH, Nové Strašecí in the Czech Republic) were used for the production of lime-based matrix specimens. All lime-based mixtures had also the same water to binder (lime and metakaolin) ratio equal to about 1.16. Three sample types were prepared: reference material without reinforcement (LR), and two reinforced mixtures with untreated (LF) and plasma treated (LFP) fibers. Fiber concentration was 2.25 wt. % of the mixture. Composition of all mixtures is summarized in **Table 2.**

Table 2 Weight concentrations of individual components in the studied mortars

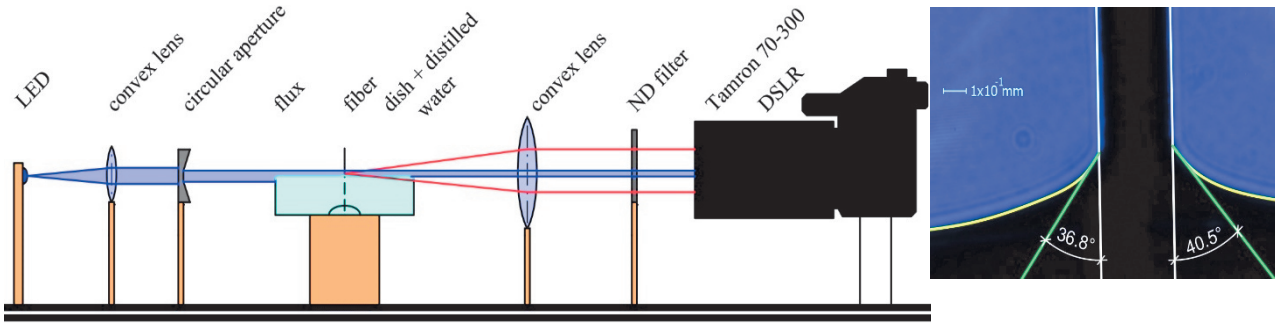
Mixture	Lime CL 90 [wt. %]	Metakaolin PKH [wt. %]	Sand ST2 [wt. %]	Sand STJ25 [wt. %]	Water [wt. %]	Plasticizer [wt. %]	MFR [wt. %]	Glass fiber types
LR	14.54	4.85	35.85	22.29	22.47	0	0	-
LF	14.15	4.72	34.90	21.70	21.90	0.38	2.25	untreated
LFP	14.15	4.72	34.90	21.70	21.90	0.38	2.25	treated

2.4. Plasma surface modifications

To improve the wettability of PET or glass fibers, oxygen treatment in inductively coupled plasma system (13.56 MHz Femto PCCE, Diener electronic GmbH) was done. Plasma treatment process parameters were: total power 100 W, total gas pressure 110 Pa, 17 sccm O_2 flow, and the exposition time 8 min.

2.5. Contact angle measurement

Direct horizontal method allowing contact angle measurement on fiber submerged in liquid (distilled water) was used. Both, as received and treated PET and glass fibers, were placed vertically into a distilled water. One part of the fibers was anchored to a bottom of a funnel, second part was protruded above the water level. The contact angle value was averaged from 6 independent measurements. Water adhering on fiber surfaces was documented by a DSLR camera having APS-C sensor and Tamron lens with 300 mm focus. A special optical setup allowing the focus on the fiber and its enlargement was located between the camera and observed fiber. The exposed fiber was illuminated by LED. The images were imported into Allplan 2015 software where the contact angle was evaluated. The scheme of the optical system is illustrated in **Fig. 1a** and image captured by DSLR is shown in **Fig. 1b.**



a) Optical system b) Fiber captured by DSLR

Fig. 1 Scheme of optical system and image captured by DSLR

2.6. SEM

Scanning electron microscope (Zeiss Merlin, Carl Zeiss Microscopy GmbH) was used for surface analysis. To eliminate surface charging, the investigated fibers were overcoated by thin gold layer using a plasma sputtering (BOC Edward Scancoats Six). The sputtering process parameters were: deposition time 40 s, sputter voltage 1.3 kV, electric current 35 mA, total gas pressure 26.6 Pa. The thickness of gold layer was ca. 10 nm as measured by Veeco DekTak 150.

2.7. Four-point bending tests

For each mixture type (cement and lime-based), five prismatic specimens were tested after 28 days of curing. Lime-based mortars were stored for 28 days at room temperature and relative humidity of about 65 %, while the cement pastes were stored in water bath. The specimen dimensions were equal to 40 × 40 × 160 mm. The testing was carried out using a press Heckert FP 100. The bending tests were displacement-controlled at a constant rate of 0.3 mm/s. Two shift sensors Essa were used for displacement monitoring. The span between supports (the diameter was equal 11 mm) was 120 mm and 60 mm between the movable supports that loaded the specimens.

3. RESULT AND DISCUSSION

Contact angle measurements revealed 66.5 ± 13.5° on untreated PET fibers. In the case of untreated glass fibers, the contact angle was equal to 78.9 ± 9.0°. After oxygen plasma treatment, the measured contact angles decreased to 24.0 ± 2.0° and 57.9 ± 7.0° for PET and glass fibers, respectively. Contact angle measurements clearly confirm the perceptible improvements of fiber hydrophilicities, as shown in **Fig. 2.**

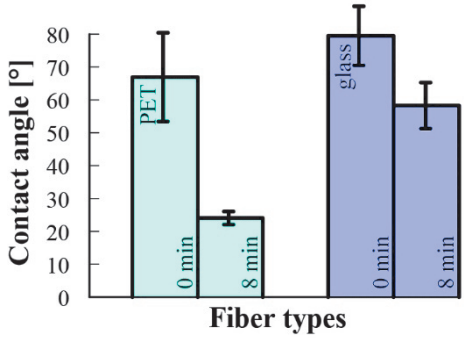


Fig. 2 Contact angle measured on PET and glass fibers

The influence of the oxygen plasma treatment on the surface morphology of PET and glass fibers is shown in **Fig. 3**. The SEM images show significant changes of PET fibers. Untreated PET fibers had smooth planar surface, while oxygen treatment reveals damage (etching) of the surfaces. On the other hand, glass fiber surface morphology was not modified by the plasma treatment.

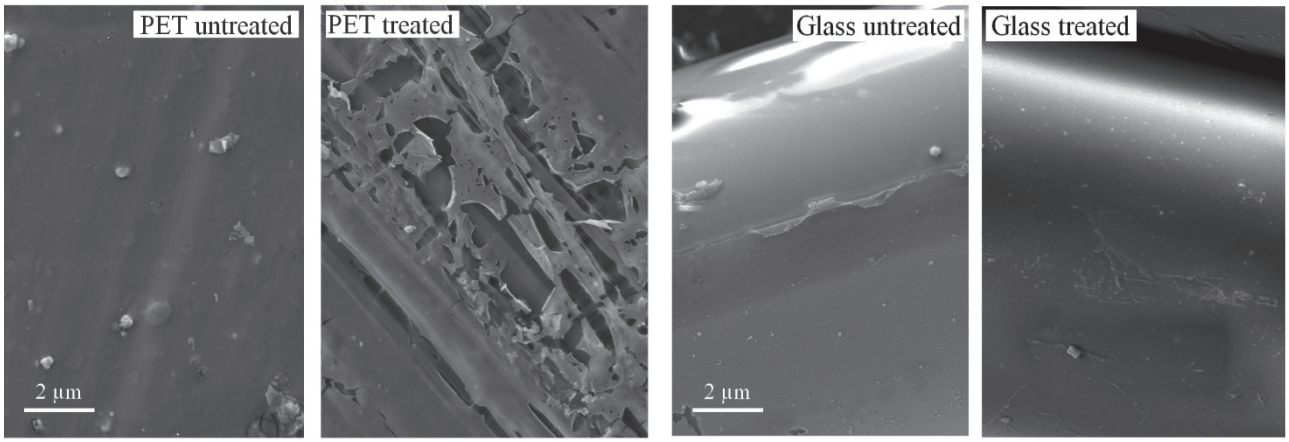


Fig. 3 SEM images of PET and glass fibers before and after the oxygen plasma treatment

Force-displacement diagrams are shown in **Figs. 4** and **5**. The maximum load-bearing capacity of cement pastes was equal to 2.90 ± 0.39 kN, 4.03 ± 0.28 kN and 3.56 ± 0.53 kN, respectively for CR, CF and CFP pastes (**Fig. 4**). In the linear phase of load-deflection curves, the maximum load-bearing capacity was the same as for CR and CF. On the other hand, CFP response parameter was equal to 2.66 ± 0.36 kN.

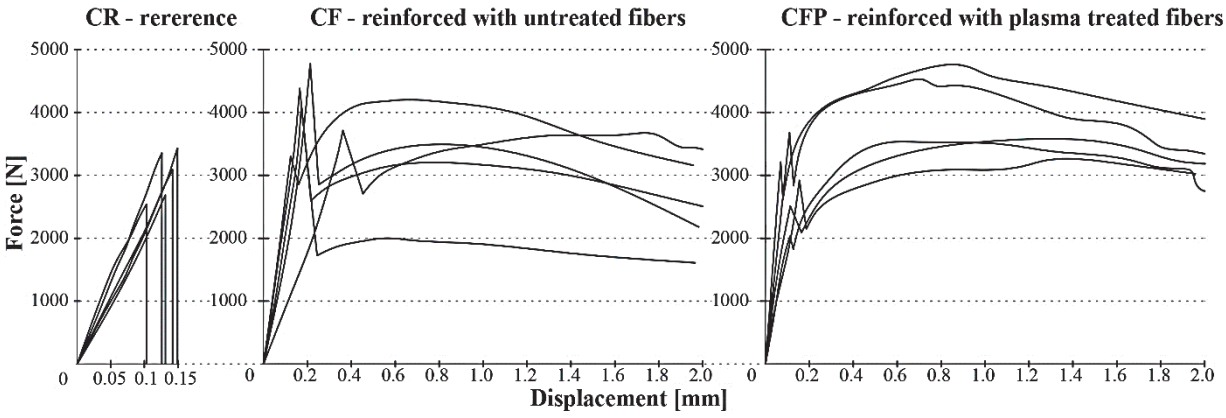


Fig. 4 Force-displacement diagrams of cement samples

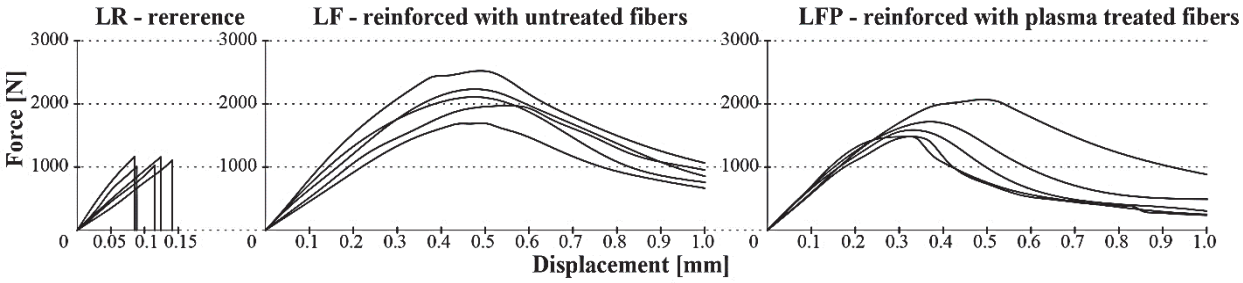


Fig. 5 Force-displacement diagrams of lime-based samples

The maximum load-bearing capacity of lime-based mortars was equal to 1.16 ± 0.06 kN, 2.08 ± 0.19 kN and 1.66 ± 0.12 kN, respectively for LR, LF and LFP mortar. The loss of maximum flexural strength of CFP (compared with CF) and LFP (compared with LF) is probably caused by fiber surface damage.

As observed, the oxygen plasma treatment significantly modified the PET fibers. In the first assumption, the fiber adhesion seems to be enhanced due to hydrophilic properties (see contact angle measurements). Next, the surface was also etched (roughened) which may additionally enhance the required adhesion. This phenomenon was expected according with other studies. [7] However, mechanical properties of such modified PET fibers may be degraded due to i) this surface damage or ii) thermally initialized modifications during the ion bombardment. Surface damage on plasma treated fibers was not so apparent in the study dealing with a treatment of PVA (polyvinyl alcohol). [12]

In contrast to the treated PET fibers, hardly seen morphological changes of glass fibers were observed after their plasma treatment. As expected, the glass fibers were resistant to oxygen plasma. To better understand the force-displacement measurements we should notice that the surface of commercially delivered glass fiber is modified by a sizing layer. This layer has to make the fiber less hydrophobic and suppress their clustering (gluing) in water suspensions. Thus, after 8 min treatment we can expect that the sizing layer was removed. Conclusive results describing exactly plasma treatment effects on interfaces adhesion must be execute in the next steps of experiments, for example by pullout tests according with other studies. [13]

Reinforced cement pastes and lime-based mortars were influenced by fiber treatments. The dependence between the force and displacement followed a linear-brittle behavior in case of CR and LR, whereas fiber reinforced samples (CF, CFP, LF and LFP) exhibited the post linear multiple cracking behavior.

Main difference between the CF and CFP samples is assigned to the force-displacement response after first cracking. The CF samples exhibited the deflection-softening behavior, while CFP samples exhibited deflection-hardening. This phenomenon is not understand. As above indicated we assume that the fiber tensile strength decreased after plasma treatment (weight loss and surface damage). Similarly, the loss of maximum flexural strength of LFP compared with LF is probably caused by removing (modifying) the sizing layer by oxygen plasma, as discussed above. Both reinforced materials exhibited slow material softening after crack localization.

4. CONCLUSION

The low temperature oxygen plasma treatment of PET and glass micro fibers increased the fiber wettability and provided better adhesion between fibers and reinforced matrix. Contact angles decreased about 60 % and 25 % for PET and glass fibers, respectively. Based on SEM, the PET fibers revealed surface damages after the plasma treatment. Bending tests pointed out changes on flexural response of both reinforced samples (i.e. cement pastes and lime-based mortars) with treated fibers in comparison with the same samples reinforced with original fibers. Cement pastes reinforced with treated PET fibers exhibited the deflection-hardening behavior, while the pastes reinforced with untreated PET fibers exhibited the deflection-softening. Both cement

pastes and lime-based mortars reinforced with plasma treated fibers showed maximum flexural strength loss up to 10 to 20 percent probably due to significant fiber surfaces damage.

ACKNOWLEDGEMENTS

This was financially supported by the Czech Science Foundation research projects 15-12420S, 14-04790S, by the Czech Technical University in Prague project SGS14/121/OHK1/2T/11 and by the EU - OP RDI project No. CZ.1.05/2.1.00/03.0091 - University Centre for Energy Efficient Buildings.

REFERENCES

[1] MALLICK P.K. Fiber-Reinforced Composites: Materials, Manufacturing, and Design, Third Edition. CRC Press: Florida, 2007.

[2] TREJBAL J., et al. The Effect of Glass Fiber Reinforcement on Flexural Strength of Lime-Based Mortars. In EAN 2015: 53rd Conference on Experimental Stress Analysis. Český Krumlov: CTU, 2015, pp. 450-453.

[3] SEPS K., VODICKA J. Fibre Reinforced Concrete with Recycled Concrete and Insulation Material STERED. Special Concrete and Composites, Vol. 1054, 2014, pp. 162-266.

[4] LIN Z., LI V.C. Crack Bridging in Fiber Reinforced Cementitious Composites with Slip-Hardening Interfaces. Journal of the Mechanics and Physics of Solids, Vol. 45, 1991, pp. 763-787.

[5] BARTOŠ J., et al. Posibilities of Modification PET Microfibers Surface Layer to Improve their Cohesion with Cement Matrix. In NANS 2014: 3rd Conference on Nanomateriály a Nanotechnologie ve Stavebnictví. Praha: CTU, 2014, pp. 8-11.

[6] TREJBAL J., et al. Modification of Surface of Reinforced Glass Fibres for the Purpose of Used in Reinforcement of Mortars. In NANS 2014 3rd Conference on Nanomateriály a Nanotechnologie ve Stavebnictví. Praha: CTU, 2014, pp. 144-151.

[7] CHEN P. Influence of Fiber Wettability on the Interfacial Adhesion of Continuous Fiber-Reinforced PPESK Composite. Journal of Applied Polymer Science, Vol. 102, 2006, pp. 2544-2551.

[8] ELSAKA S.E. Influence of Chemical Surface Treatments on Adhesion of Fiber Posts to Composite Resin Core Materials. Dental materials, Vol. 29, 2013, pp. 550-558.

[9] COKELILER D., et al. Modification of Glass Fibers to Improve Reinforcement: A plasma polymerization technique. Dental materials, Vol. 23, 2007, pp. 335-342.

[10] KIM M.T., et al. Study on an Oxygen Plasma Treatment of a Basalt Fiber and its Effect on the Interlaminar Fracture Property of Basalt/Epoxy Woven Composites. Composites: Part B, Vol. 42, 2011, pp. 499-504.

[11] WU H.Ch., LI V.C. Fiber/Cement Interface Tailoring With Plasma Treatment, Cement and Concrete Composites, Vol. 21, 1999, pp. 205-212.

[12] FELEKOGLU B. et al. A Comparative Study on the Flexural Performance of Plasma Treated Polypropylene Fiber Reinforced Cementitious Composites, Materials Processing Technology, Vol. 209, 2009, pp. 5133-5144.

[13] CECH V., et al. A Fiber-Bundle Pull-Out Test for Surface Modified Glass Fibers in GF/Polyester Composite, Compos interface, Vol. 18, 2011, pp. 309-322.